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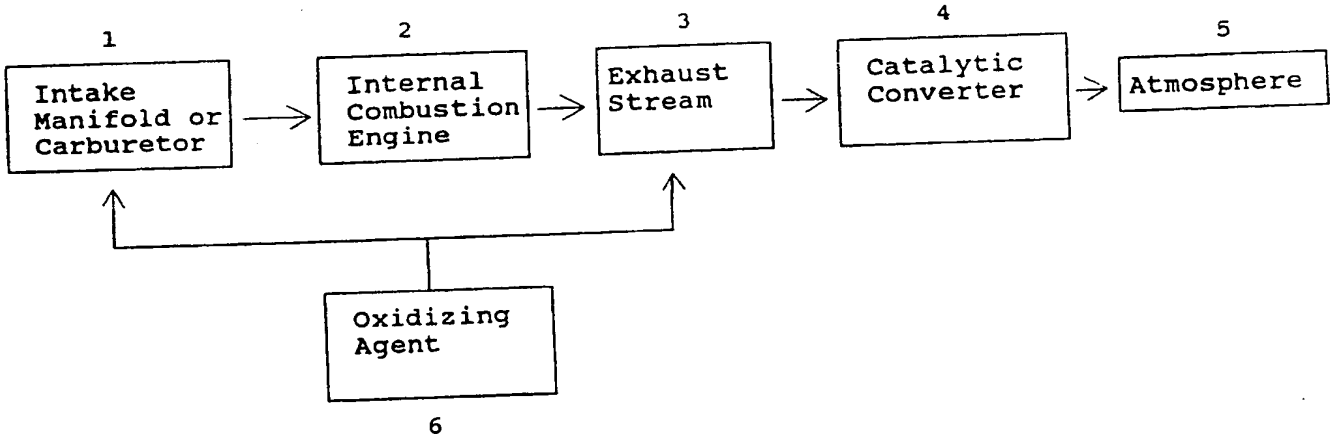
(54) Title: AUTOMOBILE CATALYTIC-CONVERTER REJUVENATION BY OXIDATION



(57) Abstract

A method and device for rapid *in situ* rejuvenation of an automobile catalytic converter catalyst by oxidation are disclosed The method comprises the injection of the oxidizing agent (6) into the automobile air stream at a point upstream of the catalytic converter (4) preferably into the intake manifold (1), and while the converter (4) is at operating temperature. The oxidizing agen (6) is preferably oxygen-enriched air or substantially purified oxygen. The device comprises an oxidizing agent supply and injection means.

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AUTOMOBILE CATALYTIC-CONVERTER REJUVENATION BY OXIDATION

RELATEDNESS OF THE APPLICATION

This application is a continuation-in-part of U.S. Serial No. 07/537,917, filed June 13, 1990.

FIELD OF THE INVENTION

This invention relates to a method of rejuvenating catalytic materials in an automobile catalytic converter and particularly the rejuvenation of the catalyst using oxidizing agents.

DESCRIPTION OF PRIOR ART

State emissions and fuel economy statutes or regulations require the periodic testing of the efficiency of automobile emission systems. When an emission system does not meet the prescribed standards, a new catalytic converter and/or a tune-up procedure is usually required. A new catalytic converter may cost hundreds of dollars. The cost of a tune-up varies considerably, but typically costs about $50.00 to $300.00.

Automobile catalytic converters become less effective by contact with lead-containing gasoline, by poorly adjusted ignition systems, by overheating and/or by

physical damage. The formation of catalyst alloys or the deposit of carbonaceous or hydrocarbon materials on the catalyst can inhibit the catalyst's ability to catalyze the oxidation of hydrocarbons, carbonaceous material or carbon monoxide, or to catalyze the reduction of oxides of nitrogen.

There have been a several methods developed for reactivating catalysts composed of noble metals on substrate using halogen-containing materials. These generally have more than one step, use expensive reagents and require fairly long treatment periods. U.S. Patent Number 3,950,491 describes a method of reactivating deactivated noble-metal catalysts used in oxidizing carbon monoxide and hydrocarbons in exhaust gas of automobiles by subjecting the deactivated catalyst to a carbonyl halide or a mixture of carbon monoxide and halogen gas at elevated temperatures (400°F to 1100°F). Example 1 demonstrates that a mixture of carbon monoxide and chlorine passing through a deactivated catalyst for one hour effects a 98% conversion of a CO at 500°F and 90% conversion of hydrocarbons at 550°F. The catalyst may be removed from the catalytic-converter chamber or applied directly to the chamber without removal from the automobile if the chamber design permits. U.S. Patent Number 3,134,732 describes a method of reactivating a platinum hydroforming catalyst, platinum on alumina, by contact with oxygen to burn off carbonaceous deposits, then to reducing platinum crystallite size with gaseous halogen, followed by a reduction step using hydrogen whereby the catalyst is regenerated. The hydroforming function involves treatment of naphtha stock in the presence of hydrogen. U.S. Patent Number 2,906,702 describes another method using a gaseous halogen to reactivate platinum-alumina hydroforming catalyst which comprises the steps of contacting the catalyst with halogen, followed by removal of volatile or

soluble halogen derivatives by steam or other aqueous medium.

However, no method is known that describes the in situ rejuvenation of automobile converter catalyst by oxidation of deposited contaminants such as carbonaceous and hydrocarbon material in an abbreviated, one step process that utilizes a single oxidizing agent.

SUMMARY OF THE INVENTION

The present invention comprises a method and device for the efficient in situ rejuvenation of the catalyst of automobile catalytic converters by oxidation of hydrocarbons and/or carbonaceous or other matter deposited on the catalyst. The rejuvenation is accomplished by introducing the oxidizing agent upstream or ahead of the catalytic converter in the automobile air stream while the engine is in operation. The duration of treatment of catalyst with oxidizing agent is sufficient to partially or completely oxidize deposited hydrocarbons and/or carbonaceous or other materials. In one embodiment of the process, the oxidizing agent is introduced into the exhaust stream just upstream of the converter. In a second embodiment of the process, the oxidizing agent is introduced into the intake manifold or carburetor of the internal combustion engine. When the oxidizing agent reaches the catalytic converter, the hydrocarbons and/or carbonaceous material deposited on the catalyst are partially or completely oxidized, rendering the catalyst more effective.

The present invention also provides a method for reducing carbon monoxide and hydrocarbon emissions from automobiles by contacting the catalytic converter catalyst with an oxidizing agent under operating conditions for a period of time sufficient to decrease carbon monoxide and hydrocarbon emissions. In addition to reducing carbon

monoxide and hydrocarbon emissions, said method can also increase carbon dioxide emissions. As is known to those of skill in the art, a decrease in carbon monoxide and increase in carbon dioxide emissions can reflect an improvement in gasoline mileage.

The device comprises a means for injecting the oxidizing agent into the automobile air stream at a point upstream of the catalytic converter. In one embodiment, the oxidizing agent is injected into the exhaust stream just upstream of the converter by way of a fitting inserted into an exhaust line hole. In a second embodiment, the oxidizing agent is injected by way of a fitting into the intake manifold or into a vacuum line feeding directly into either the intake manifold or the carburetor. The oxidizing agent supply comprises an oxidizing agent in a vessel and a means of delivery of the agent to the fitting or injection means.

The present invention provides a simple, inexpensive alternative to replacement of spent automobile catalytic converters. Further, the subject catalyst regeneration process requires only a brief treatment period and uses relatively inexpensive reagents.

BRIEF DESCRIPTION OF THE DRAWING

Figure 1 is a schematic diagram of two embodiments of the method of the subject invention in which the oxidizing agent is injected into the automobile air stream at the exhaust stream or the intake manifold or carburetor.

DETAILED DESCRIPTION OF THE INVENTION

The subject inventive process and device can be used to rejuvenate all automobile catalytic converter catalysts regardless of the composition of the catalyst or the catalyst support or substrate. It is not believed,

however, that the subject method can remove lead from lead-contaminated catalytic converter.

The subject method for rejuvenation of the catalyst is carried out by the introduction of an oxidizing agent into the automobile air stream, such that the agent contacts and oxidizes the converter catalyst and contaminants (e.g., hydrocarbons and carbonaceous materials) contained thereon. The resulting oxidation products, such as carbon dioxide and water, are then exhausted into the atmosphere.

The subject method of catalyst regeneration and decrease in carbon monoxide and hydrocarbon emissions is carried out while the automobile and its converter are in operation and the catalytic converter remains mounted on the automobile (in situ). The operating temperature inside a catalytic converter can vary substantially, but is at least about 500°F, and typically is between about 800° and 1400°F. With the catalytic converter in place in the automobile and the engine running, an oxidizing agent is introduced ahead of the converter so that the contaminants on the catalyst can be oxidized and resulting oxidation products can then exit through the exhaust system.

According to the subject methods, the oxidizing agent is introduced into the automobile air stream, wherein the oxidizing agent is heated and dispersed or mixed in said stream prior to entry of the oxidizing agent into the catalytic converter and contact with the catalyst or contaminants thereon. "Automobile air stream" means the flow or stream of air through the air intake manifold, carburetor, vacuum lines, internal combustion engine, exhaust conduits, catalytic converter and any intermediate conduit, device or apparatus.

The oxidizing agent is a material which rapidly oxidizes the deposited contaminants under typical catalytic

converter operating conditions. Such agents include, but are not limited to substantially pure oxygen or oxygen-enriched air. "Oxygen-enriched air" means air having an oxygen concentration greater than about 30% (v/v). It is increasingly preferred that the oxygen-enriched air contain 50%, 70%, 80% and 90% (v/v) oxygen. "Substantially pure oxygen" means at least about 95% (v/v) oxygen. The use of substantially pure oxygen in the subject methods is most preferred. The advantages of using substantially pure oxygen include: (1) less than 5% (v/v) nitrogen is introduced into the converter; (2) the use of substantially pure oxygen reduces the catalyst treatment time; and (3) substantially pure oxygen is less expensive per mole and less hazardous than halide oxidizing agents such as chlorine.

The duration of treatment is determined by the type and concentration of oxidizing agent used, the flow or feed rate of oxidizing agent into the automobile air stream, the operating temperature of the automobile and other factors. The duration of treatment is sufficient to partially or completely regenerate the catalyst or to cause a positive reduction in the emission of carbon monoxide and/or hydrocarbons. When enriched air or substantially pure oxygen is used as the oxidizing agent, it has been observed that the duration of treatment is typically between about 2 and 30 minutes, and preferably between about 5 and 15 minutes. A "partial regeneration" of the catalyst means a reduction of the carbon monoxide and/or hydrocarbon emission by at least about 5%. A "positive reduction" in the emission of carbon monoxide and/or hydrocarbons means a reduction of either or both emissions by at least about 5%. It is increasingly preferred that the reduction in said emissions be at least about 10%, 25%, 50%, 75%, 90% and 95%. Such reductions in emissions can be measured, for example, by a Sun Modular Engine Analyzer (MEA).

As exemplified herein, using 95% (v/v) oxygen as an oxidizing agent, and a flow rate of about 8-18 liters/minute through an 1/8 inch fitting into the intake manifold, it has been found that a treatment time of about 15 minutes is sufficient to produce significant reductions of hydrocarbon and carbon monoxide emissions. However, it has also been found that flow rates as low as 2 liters/minute can regenerate slightly to moderately contaminated converter catalyst in less than about 30 minutes.

In accordance with federal and/or state laws, the subject invention does not require or involve any modification to or tampering with the catalytic converter itself.

Figure 1 schematically illustrates two embodiments of the subject invention. The oxidizing agent (6) can be introduced into the automobile air stream at the intake manifold or carburetor (1) or in the exhaust stream (3) upstream of the converter (4). In the former embodiment, the oxidizing agent can be introduced by an injection means into a vacuum line that feeds into the intake manifold or into the carburetor. Such injection means can be a plastic fitting. In the latter embodiment, a hole or tap is drilled into the exhaust conduit and the oxidizing agent is introduced by an injection means, such as a stainless steel fitting, into the exhaust conduit. In the Examples herein, a 1/8 inch fitting has been found to be suitable. It is preferred that the oxidizing agent be introduced into the carburetor or intake manifold or vacuum lines which feed directly thereto. This embodiment is preferred because it is not necessary to hoist the automobile to gain access to the air stream; it does not require the drilling and repair of a hole or tap in the exhaust conduit or introduce the possibility of an exhaust leak; and it provides for more

complete heating of the oxidizing agent prior to contact with the catalyst or contaminants thereon.

The subject device used in catalyst rejuvenation or in carbon monoxide and hydrocarbon emission reduction comprises an oxidizing agent supply and an injection means for introducing the supply's oxidizing agent to the automobile's air stream. The point of injection into the air stream can be at a number of locations along the automobile air stream. Depending on the temperature at the point of injection, plastic or stainless steel fittings can be used as the injection means. The oxidizing agent supply is a vessel that contains oxidizing agent and is capable of delivering the agent to the injection means. For example, a 95% (v/v) compressed oxygen tank or an oxygen concentrator can supply a stream of substantially pure oxygen to the injection means. The means of delivery of the oxidizing agent by the supply vessel can be by any means known in the art including mechanical pumping or channeling of compressed oxidizing agent. The oxidizing agent supply can be constructed to provide an appropriate flow rate of oxidizing agent that efficiently rejuvenates the converter catalyst or reduces emissions. For example, the oxidizing agent supply can provide means of selecting flow rate according to the engine size, number of cylinders of the automobile to be treated, the condition of the catalyst as reflected by the total mileage of the automobile, or other factors. It is a matter of experimentation to determine an appropriate flow rate of a particular oxidizing agent to provide for an efficient regeneration of the converter catalyst or reduction in hydrocarbon and carbon monoxide emissions.

EXAMPLES

Example 1

A tap was drilled into each exhaust pipe of about 50 automobiles between the engine and the catalytic converter. After each engine had run for fifteen minutes and had heated the catalyst, 95% (v/v) oxygen was injected into the tap at a rate of about 13 liters/minute for five minutes while the engine was still in operation. Gases passed out through the exhaust into the atmosphere. The emissions were tested before and after the oxygen injection, and all catalytic converters tested showed a minimum of 25% improvement in the standard hydrocarbon and carbon monoxide State of Colorado Vehicle Emissions Control System Tests.

Example 2

Following the procedure of Example 1, another test produced the results below. "HC" refers to hydrocarbons.

Tailpipe Emissions at Idle

	Standard	Before	After
CO%	1.50	1.22	0.04
HC ppm	400	169	47

Tailpipe Emissions at 2500 RPM

	Standard	Before	After
CO%	1.50	8.98	0.07
HC ppm	400	420	40

Example 3

The procedure of Example 1 was followed with the exception that the 95% oxygen was introduced into the intake manifold of a 1985 Mercedes (8 cylinders). The flow rate of oxygen provided by the oxygen concentrator was between about 8 and 18 liters/minute through the 1/8 inch fitting. The treatment procedure was as follows: 5 minutes of oxygen at elevated rpm (about 2500 rpm), 5

minutes of oxygen at idle, followed by 5 minutes of oxygen at elevated rpm (about 2500 rpm). The following results were measured using a Sun Modular Engine Analyzer.

Before Treatment

RPM	654	RPM
HC	254	PPM
CO	1.12	%
O2	0.6	%
CO2	14.48	%

During Treatment--Elevated RPM

RPM	2410	RPM
HC	0	PPM
CO	0.00	%
O2	0.2	%
CO2	15.96	%

After Treatment

RPM	651	RPM
HC	0	PPM
CO	0.00	%
O2	0.6	%
CO2	16.45	%

Example 4

The procedure of Example 3 was used on a 1981 Jeep and the following results were obtained.

Before Treatment

RPM	727	RPM
HC	238	PPM
CO	2.41	%
O2	5.9	%
CO2	8.66	%

During Treatment--Elevated RPM

RPM	2016	RPM
HC	40	PPM
CO	0.11	%
O2	5.8	%
CO2	10.86	%

During Treatment--Idle

RPM	824	RPM
HC	50	PPM
CO	0.10	%
O2	6.5	%
CO2	11.20	%

After Treatment

RPM	1581	RPM
HC	47	PPM
CO	0.12	%
O2	5.8	%
CO2	10.80	%

Example 5

The procedure of Example 3 was used on a 1990 Ford Econoline and the following results were obtained.

Before Treatment

RPM	689	RPM
HC	238	PPM
CO	0.55	%
O2	0.9	%
CO2	14.23	%

During Treatment--Elevated RPM

RPM	2619	RPM
HC	15	PPM
CO	0.00	%
O2	7.8	%
CO2	9.59	%

During Treatment--Idle

RPM	675	RPM
HC	22	PPM
CO	0.00	%
O2	9.1	%
CO2	9.77	%

After Treatment

RPM	0	RPM
HC	36	PPM
CO	0.00	%
O2	0.1	%
CO2	15.52	%

Example 6

The procedure of Example 3 was used on a 1982 Mitsubishi Cordia (4 cylinders) and the following results were obtained.

Before Treatment

RPM	1062	RPM
HC	210	PPM
CO	3.05	%
O2	9.6	%
CO2	5.81	%

During Treatment--Elevated RPM

RPM	2508	RPM
HC	52	PPM
CO	0.07	%
O2	0.9	%
CO2	15.18	%

After Treatment

RPM	1183	RPM
HC	38	PPM
CO	0.69	%
O2	9.0	%
CO2	8.84	%

While various embodiments of the present invention have been described in detail, it is apparent that modifications and adaptations will occur to those skilled in the art. However, it is to be expressly understood that such modifications and adaptations are within the spirit and scope of the present invention, as set forth in the following claims.

CLAIMS

1. A method for in situ regeneration of automobile catalytic converter catalyst so as to decrease hydrocarbon and carbon monoxide emissions, comprising the step of:

   (a) contacting an oxidizing agent with said catalyst and contaminants deposited thereon at catalytic converter operating temperatures.

2. The method of claim 1, wherein said oxidizing agent is selected from the group consisting of oxygen-enriched air and substantially pure oxygen.

3. The method of claim 2, wherein said oxidizing agent is delivered by an oxidizing agent supply at a flow rate of between about 2 and about 18 liters/minute through a 1/8 inch diameter orifice.

4. The method of claim 1, wherein the duration of said contacting step is at between about 2 and about 30 minutes.

5. The method of claim 4, wherein said duration is between about 5 and about 15 minutes.

6. The method of claim 1, wherein said oxidizing agent is contacted with said catalyst and deposits by introducing said agent into the exhaust stream immediately upstream of the catalytic converter.

7. The method of claim 1, wherein said oxidizing agent is contacted with said catalyst and deposits by introducing said agent into the intake manifold or carburetor.

8. A device for in situ regeneration of an automobile catalytic converter catalyst at converter operating

temperatures comprising an oxidizing agent supply and an injection means, wherein said injection means communicates said supply's oxidizing agent to the automobile air stream.

9. The device of claim 8, wherein said injection means comprises a fitting.

10. The device of claim 8, wherein said oxidizing agent is selected from the group consisting of oxygen-enriched air and substantially pure oxygen.

11. The device of claim 10, wherein said oxidizing agent supply delivers oxidizing agent at a flow rate of between about 2 and about 18 liters/minute though an 1/8 inch diameter injection means.

12. The device of claim 8, wherein said injection means delivers oxidizing agent to said air stream at an intake manifold or carburetor.

13. The device of claim 8, wherein said injection means delivers oxidizing agent to said air stream at an exhaust stream.

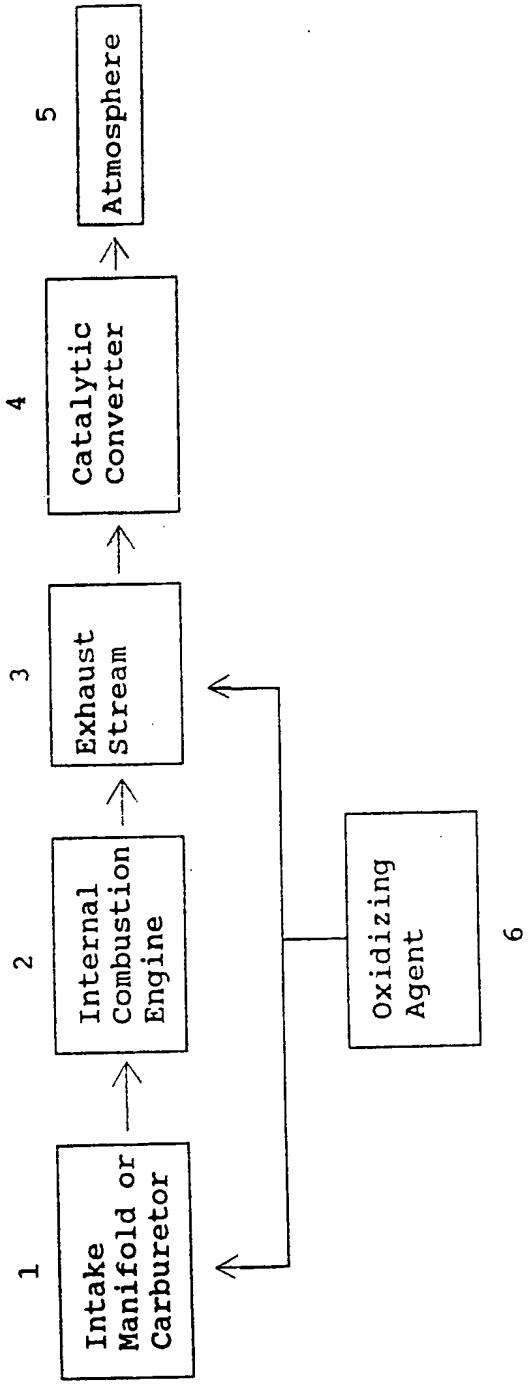
1
Intake Manifold or Carburetor
2
Internal Combustion Engine
3
Exhaust Stream
4
Catalytic Converter
5
Atmosphere
6
Oxidizing Agent

FIGURE 1

INTERNATIONAL SEARCH REPORT

International Application No. PCT/US91/04221

I. CLASSIFICATION OF SUBJECT MATTER (if several classification symbols apply, indicate all) [6]

According to International Patent Classification (IPC) or to both National Classification and IPC

IPC(5): F01N 3/22, 3/34

U.S Cl: 422/178, 168, 173; 60/274, 282, 283, 285

II. FIELDS SEARCHED

Minimum Documentation Searched [7]

Classification System	Classification Symbols
U.S	422/168, 173, 178 60/273, 274, 282, 283, 285

Documentation Searched other than Minimum Documentation to the Extent that such Documents are Included in the Fields Searched [8]

III. DOCUMENTS CONSIDERED TO BE RELEVANT [9]

Category *	Citation of Document, [11] with indication, where appropriate, of the relevant passages [12]	Relevant to Claim No. [13]
Y	US, A, 4,372,111 (VIRK ET AL) 08 February 1983. See Column 1, lines 57-64.	1-6 8-11 and 13
Y	US, A, 4,331,454 (SWEENEY) 25 May 1982. See entire disclosure.	1-13
Y	US, A, 3,979,185 (STEVENSON) 07 September 1976. See column 1, lines 42-70.	1-6
Y	US, A, 3,826,089 (NAKAJIMA ET AL.) 30 July 1974. See entire disclosure.	1-13

* Special categories of cited documents: [10]

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"&" document member of the same patent family

IV. CERTIFICATION

Date of the Actual Completion of the International Search

09 September 1991

Date of Mailing of this International Search Report

30 SEP 1991

International Searching Authority

ISA/US

Signature of Authorized Officer

Amalia L. Santiago